An Approach to Distribution Functions for Gaussian Molecules

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ABSTRACT: The distribution function $P(s)$ ds of the radius of gyration of a Gaussian molecule of arbitrary complexity is obtained as an exact series expansion through fourth order. The asymptotic behavior of $P(s)$ ds is given to within a constant and is found to depend upon the magnitude and degeneracy of the minimum eigenvalue of the Kirchhoff matrix. The distribution function of the inertial tensor is also investigated by means of a transformation to polar coordinates; the first term in the series expansion of this function is given. A proof is given for the known fact that a Gaussian molecule is never spherically symmetric in a coordinate frame affixed to the principal axes of the molecule.

Distribution functions of the radius of gyration $P(s)$ ds and of the inertial tensor $P(S^{\alpha\beta})\Pi\, \mathrm{d}S^{\alpha\beta}$ of Gaussian molecules of arbitrary complexity in the unperturbed state are here treated by a method which exposes some interesting features of these functions. The method is based on the simple observation that the radius of gyration or principal components of the inertial tensor are radial coordinates in multidimensional spaces. Transformations from Cartesian to polar coordinates make explicit the dependence of the distribution functions upon s or $S^{\alpha\beta}$.

The exact power series development of $P(s)$ ds is carried to fourth order, and the rule for computation of successively higher order terms is given. An elementary proof that an unperturbed Gaussian molecule is never spherically symmetric is given, and the first term in the expansion of $P(S^{\alpha\beta})\Pi\, \mathrm{d}S^{\alpha\beta}$ is displayed. All calculations are general with respect to the dimensionality of the space and to the connectivity of the molecule.

I. Distribution Function of the Radius of Gyration

A configuration of n points in an m dimension space may be specified by assigning values to each of the mn Cartesian coordinates of the vector $\mathbf{x} = (x_1{}^1, x_1{}^2, \ldots, x_1{}^m, x_2{}^1, \ldots, x_n{}^m)$. The space of all configurations constitutes $\mathbf{R}^{mn}$. The potential energy V/kT of a Gaussian molecule with graphical structure (connectivity) specified by the Kirchhoff matrix $\mathbf{K}$ is[1,2]

$$V/kT = \gamma \mathbf{x}(\mathbf{K} \otimes \mathbf{1}_m)\mathbf{x}'$$

where $\gamma = m/2\langle l^2\rangle$, in which $\langle l^2\rangle$ is the mean-square unperturbed length of one step, $\mathbf{1}_m$ is the identity of rank m, and $\mathbf{x}'$ is the transpose of $\mathbf{x}$. The probability distribution $P(s)$ ds is given by

$$P(s)\,\mathrm{d}s = \mathrm{d}s\, Z^{-1} \int \prod_{\alpha=1}^{m} \delta\Big(\sum_j x_j{}^\alpha\Big) \times \exp[-\gamma \mathbf{x}(\mathbf{K} \otimes \mathbf{1}_m)\mathbf{x}']\dot{x}/\mathrm{d}s \quad (1)$$

where $\dot{x}$ is the mn dimensional volume element

$$\prod_{\alpha=1}^{m} \prod_{j=1}^{n} \mathrm{d}x_j{}^\alpha$$

Z is the configuration integral (given below), and the product of delta functions fixes the origin of coordinates at the center of mass of the distribution.

The squared radius of gyration $s^2 = n^{-1}\mathbf{x}\mathbf{x}'$. A transformation of the group $O(mn)$ acting to the left on $\mathbf{x}'$ leaves s^2 invariant. In particular, the transformation $(\mathbf{T} \otimes \mathbf{1}_m)\mathbf{x}' = \mathbf{q}'$, $\mathbf{T} \in (n)$, which diagonalizes $\mathbf{K}$ according to $\mathbf{TKT}' = \boldsymbol{\Lambda}$, where $\boldsymbol{\Lambda} = \mathrm{diag}(\lambda_1, \ldots, \lambda_n)$, leaves s^2 invariant. Hence $s^2 = n^{-1}\mathbf{q}\mathbf{q}'$.

The matrix $\mathbf{K}$ always has one and only one zero eigenvalue if the graph that it describes is connected. Let $q_n{}^\alpha$ be the components of the normal coordinates which belong to the zero eigenvalue. Then

$$P(s)\,\mathrm{d}s = \mathrm{d}s\, Z^{-1} \int \prod_{\alpha=1}^{m} \delta(q_n{}^\alpha) \times \exp[-\gamma \mathbf{q}(\boldsymbol{\Lambda} \otimes \mathbf{1}_m)\mathbf{q}']\dot{q}/\mathrm{d}s \quad (2)$$

since $q_n{}^\alpha$ is proportional to $\Sigma x_j{}^\alpha$. Integration over the $q_n{}^\alpha$ amounts to deletion of the zero eigenvalue (corresponding to translation) in $\boldsymbol{\Lambda}$. Thus

$$P(s)\,\mathrm{d}s = \mathrm{d}s\, Z^{-1} \int \exp[-\gamma \mathbf{q}_0(\boldsymbol{\Lambda}_0 \otimes \mathbf{1}_m)\mathbf{q}_0']\dot{q}_0/\mathrm{d}s \quad (3)$$

where $\boldsymbol{\Lambda}_0 = \mathrm{diag}(\lambda_1, \ldots, \lambda_{n-1})$, $|\boldsymbol{\Lambda}_0| \neq 0$, and $\mathbf{q}_0$ is the $m(n-1)$ dimensional vector obtained from $\mathbf{q}$ by striking the $q_n{}^\alpha$. The configuration integral which normalizes $P(s)$ ds is easily seen to be

$$Z = \int \exp[-\gamma \mathbf{q}_0(\boldsymbol{\Lambda}_0 \otimes \mathbf{1}_m)\mathbf{q}_0']\dot{q}_0 = (\pi/\gamma)^{m(n-1)/2}|\boldsymbol{\Lambda}_0|^{-m/2} \quad (4)$$

The vector $\mathbf{q}_0$ is now converted to the polar form

$$\mathbf{q}_0 = n^{1/2}s\mathbf{u} \quad (5)$$

where all vectors $\mathbf{u}$ ($\mathbf{u}\mathbf{u}' = 1$) constitute the space $S^{m(n-1)-1}$, the $mn - m - 1$ dimensional sphere. The volume element in polar coordinates is obtained from the fact that $|\mathbf{G}|^{1/2}\dot{y}$ is the volume element of the space with metric $\mathrm{d}\sigma^2 = \mathrm{d}\mathbf{y}\, \mathbf{G}\, \mathrm{d}\mathbf{y}'$. We have

$$\mathrm{d}\sigma^2 = \mathrm{d}\mathbf{q}_0\, \mathrm{d}\mathbf{q}_0' = n(\mathrm{d}s\, \mathbf{u} + s\ \mathrm{d}\mathbf{u}) \times (\mathbf{u}'\, \mathrm{d}s + \mathrm{d}\mathbf{u}'s) = n(\mathrm{d}s^2 + s^2\, \mathrm{d}\mathbf{u}\, \mathrm{d}\mathbf{u}') \quad (6)$$

since $\mathbf{u}\, \mathrm{d}\mathbf{u}' + \mathrm{d}\mathbf{u}\, \mathbf{u}' = 2(\mathbf{u}\, \mathrm{d}\mathbf{u}') = 0$. The volume element

$$\dot{q}_0 \rightarrow n^{m(n-1)/2}s^{m(n-1)-1}\, \mathrm{d}s\, \dot{u}$$

so that eq 3, with use of eq 4, becomes

$$P(s)\,\mathrm{d}s = (n\gamma/\pi)^{m(n-1)/2}|\boldsymbol{\Lambda}_0|^{m/2}s^{mn-m-1} \times \mathrm{d}s\, F(n\gamma s^2) \quad (7\mathrm{a})$$

where

$$F(n\gamma s^2) = \int \exp[-n\gamma s^2\mathbf{u}(\boldsymbol{\Lambda}_0 \otimes \mathbf{1}_m)\mathbf{u}']\dot{u} \quad (7\mathrm{b})$$

Completion of the quadratures in this expression can be accomplished by at least three different methods.

To demonstrate the equivalence of eq 7 with conventional formulations, the condition that $\mathbf{u}$ lies on the unit sphere is imposed by insertion of $\delta(\mathbf{u}\mathbf{u}' - 1)$ in the integral analogous to eq 7, but taken over $\mathbf{R}^{m(n-1)}$. Thus

$$\int_{\mathbf{uu}'=1} \exp[-a\mathbf{u}(\Lambda_0 \otimes 1_m)\mathbf{u}']\dot{u}$$
$$= \int_{\mathbf{R}^{m(n-1)}} \exp[-a\mathbf{y}(\Lambda_0 \otimes 1_m)\mathbf{y}']\delta(\mathbf{yy}'-1)\dot{y}$$
$$= (2\pi)^{-1}(\pi/a)^{m(n-1)/2} \times \int_{-\infty}^{\infty} d\beta e^{-i\beta}|\Lambda_0 - (i\beta/a)1_{n-1}|^{-m/2}$$

and eq 7 becomes

$$P(s)\,\mathrm{d}s = (2\pi s)^{-1}|\Lambda_0|^{m/2}\,\mathrm{d}s \times \int_{-\infty}^{\infty} |\Lambda_0 - (i\beta/n\gamma s^2)1_{n-1}|^{-m/2}e^{-i\beta}\,\mathrm{d}\beta \quad (8)$$

which coincides with the result of Coriell and Jackson[3] for the one-dimensional linear chain on introduction of $\lambda_l = 4\sin^2(\pi l/2n)$.

An alternative evaluation of eq 7 is accomplished by series expansion of the integrand to give

$$P(s)\,\mathrm{d}s = (n\gamma/\pi)^{m(n-1)/2}|\Lambda_0|^{m/2}s^{mn-m-1}\,\mathrm{d}s \times \sum_{p=0}^{\infty}[(-n\gamma s^2)^p/p!]\int_{\mathbf{uu}'=1}[\mathbf{u}(\Lambda_0 \otimes 1_m)\mathbf{u}']^p\dot{u} \quad (9)$$

Since

$$\int_{\mathbf{uu}'=1}\dot{u} = 2\pi^{m(n-1)/2}/\Gamma[m(n-1)/2] \quad (10)$$

the first term of the series in eq 9 is

$$2(n\gamma)^{m(n-1)/2}|\Lambda_0|^{m/2}s^{mn-m-1}/\Gamma[m(n-1)/2]$$

which is exact, and so improves the previous results of Fixman,[4] Norisuye and Fujita,[5] Forsman,[6] and Coriell and Jackson.[3]

The integral

$$F(t,p) = \int_{S^{t-1}}(\mathbf{u}_t\mathbf{A}_t\mathbf{u}_t')^p\dot{u}_t, \quad \mathbf{A}_t = \mathrm{diag}(a_1, a_2, \ldots, a_t)$$

over all $\mathbf{u}_t$ such that $\mathbf{u}_t\mathbf{u}_t' = 1$ is evaluated by a recursive method. Let $\mathbf{u}_t = (\cos\theta_{t-1}, \sin\theta_{t-1}\mathbf{u}_{t-1})$, so that $d\sigma^2 = \mathrm{d}\mathbf{u}_t\,\mathrm{d}\mathbf{u}_t' = \mathrm{d}\theta_{t-1}^2 + \sin^2\theta_{t-1}\,\mathrm{d}\mathbf{u}_{t-1}\,\mathrm{d}\mathbf{u}_{t-1}'$, and $\dot{u}_t = \sin^{t-2}\theta_{t-1}\,\mathrm{d}\theta_{t-1}\dot{u}_{t-1}$.

The integral becomes

$$F(t,p) = \sum_{q=0}^{p}\binom{p}{q}a_t^{p-q}\int_0^{\pi}(\sin\theta_{t-1})^{2q+t-2} \times (\cos\theta_{t-1})^{2p-2q}\,\mathrm{d}\theta_{t-1}\int_{S^{t-2}}(\mathbf{u}_{t-1}\mathbf{A}_{t-1}\mathbf{u}_{t-1}')^q\dot{u}_{t-1}$$
$$= \sum_{q=0}^{p}\frac{\Gamma(p+1)\Gamma(q+t/2-1/2)\Gamma(p-q+1/2)}{\Gamma(q+1)\Gamma(p-q+1)\Gamma(p+t/2)} \times a_t^{p-q}F(t-1,q) \quad (11a)$$

with

$$F(t,0) = 2\pi^{t/2}/\Gamma(t/2); \quad F(2,1) = \pi(a_1+a_2) \quad (11b)$$

By application of eq 11 one finds

$$F(t,1) = \frac{\pi^{t/2}}{\Gamma(t/2+1)}\mathrm{Tr}(A_t) \quad (12a)$$

$$F(t,2) = \frac{\pi^{t/2}}{\Gamma(t/2+2)}[\mathrm{Tr}(A_t^2) + (\tfrac{1}{2})\mathrm{Tr}^2(A_t)] \quad (12b)$$

$$F(t,3) = \frac{\pi^{t/2}}{\Gamma(t/2+3)}[2\mathrm{Tr}(A_t^3) + \tfrac{3}{2}\mathrm{Tr}(A_t^2)\mathrm{Tr}(A_t) + \tfrac{1}{4}\mathrm{Tr}^3(A_t)] \quad (12c)$$

Use of these expressions in eq 9, with $\mathrm{Tr}(A_t^k) = \mathrm{Tr}(\Lambda_0^k \otimes 1_m) = m\mathrm{Tr}(\Lambda_0^k)$, gives the first four terms in the expansion of $P(s)$ ds. The general term $F(t,q)$ of the set of eq 12 is evidently of the form

$$F(t,q) = \frac{\pi^{t/2}}{\Gamma(t/2+q)}\Sigma b_q(k_1, k_2, \ldots, k_l) \times \mathrm{Tr}(A_t^{k_1})\ldots\mathrm{Tr}^l(A_t^{k_l})$$

where the sum is over all sets $\{k\}$ such that

$$\sum_{j=1}^{l} jk_j = q$$

Substitution of an expression of this form for $F(t,p)$ and $F(t-1,p)$ in eq 11a yields a set of linear equations to be solved for the b_q in terms of lower order $b_{q'}$; by this method eq 12 were obtained.

The third method of evaluation of the integral defined by eq 7b gives the asymptotic expansion of $P(s)$ ds as $s \to \infty$. Preliminary direct evaluation of

$$F(a) = \int \exp[-a\mathbf{u}(\Lambda_0 \otimes 1_m)\mathbf{u}']\dot{u} \quad (7b)$$

suggests that the degeneracy of $\Lambda_0 \otimes 1_m$ must first be removed. Let Λ_p ($p \leq n-1$) be the matrix of all distinct and ordered eigenvalues of Λ_0. The jth eigenvalue of Λ_p occurs ω_j times in Λ_0, and $m\omega_j$ times in $\Lambda_0 \otimes 1_m$. Now define $\mathbf{u} = (v_j\mathbf{t}_j)$, where v_j is a scalar and $\mathbf{t}_j$ ($1 \leq j \leq p$) lies on the $m\omega_j - 1$ dimensional sphere, so that

$$\mathbf{u}(\Lambda_0 \otimes 1_m)\mathbf{u}' = \mathbf{v}\Lambda_p\mathbf{v}' \quad (13)$$

The volume element $\dot{u}$ is converted to $\mathbf{v}$ and $\mathbf{t}_j$ space by the usual method. We have

$$\mathrm{d}\mathbf{u}\,\mathrm{d}\mathbf{u}' = \sum_{j=1}^{p}(\mathrm{d}v_j^2 + v_j^2\,\mathrm{d}\mathbf{t}_j\,\mathrm{d}\mathbf{t}_j')$$

so that

$$\dot{u} = \prod_{j=1}^{p}\dot{t}_j v_j^{m\omega_j-1}\,\mathrm{d}v_j$$

Integrals over the t_j give

$$\int \Pi\dot{t}_j = \prod_{j=1}^{p}2\pi^{m\omega_j/2}/\Gamma(m\omega_j/2) = C$$

and $F(a)$ reduces to

$$F(a) = C\int_{\mathbf{vv}'=1}\exp[-a\mathbf{v}\Lambda_p\mathbf{v}']\prod_{j=1}^{p}v_j^{m\omega_j-1}\,\mathrm{d}v_j \quad (14)$$

taken over the $p-1$ dimensional sphere.

Use is now made of projective geometry to remove the restrictions on the ranges of integration. The antipodal projection of S^{p-1} onto the $p-1$ dimensional hyperplane is defined by the coordinate transformation[7,8]

$$x_i = v_i/v_p \quad (1 \leq i \leq p-1)$$

Thus, $1 + \mathbf{xx}' = v_p^{-2}$ and the metric

$$\mathrm{d}\mathbf{v}\,\mathrm{d}\mathbf{v}' = (1+\mathbf{xx}')^{-1}\,\mathrm{d}\mathbf{x}(\mathbf{1}+\mathbf{x}'\mathbf{x})^{-1}\,\mathrm{d}\mathbf{x}'$$

is obtained from

$$\mathrm{d}\mathbf{v}\,\mathrm{d}\mathbf{v}' = \mathrm{d}\overline{\mathbf{v}}\,\mathrm{d}\overline{\mathbf{v}}' + \mathrm{d}v_p^2$$

and

$$\mathrm{d}\mathbf{x} = v_p^{-1}(\mathrm{d}\overline{\mathbf{v}} - v_p^{-1}\,\mathrm{d}v_p\overline{\mathbf{v}})$$

[Use is made of $(\mathbf{1}+\mathbf{x}'\mathbf{x})^{-1} = \mathbf{1} - \mathbf{x}'(1+\mathbf{xx}')^{-1}\mathbf{x} = \mathbf{1} - \overline{\mathbf{v}}'\overline{\mathbf{v}}$

which follows from $\mathbf{x}(1 + \mathbf{x}'\mathbf{x})^{-1} = (1 + \mathbf{x}\mathbf{x}')^{-1}\mathbf{x}$.] The restriction of $\Pi\, \mathrm{d}v_j$ to $\mathbf{v}\mathbf{v}' = 1$ is equivalent to

$$(1 + \mathbf{x}\mathbf{x}')^{-p/2} \prod_{j=1}^{p-1} \mathrm{d}x_j$$

taken over $1 + \mathbf{x}\mathbf{x}' > 0$, or $-\infty \le x_i \le \infty$. The integral of eq 14 now becomes

$$F(a) = C \int \exp\left[-a\frac{\lambda_p + \mathbf{x}\Lambda_{p-1}\mathbf{x}'}{1 + \mathbf{x}\mathbf{x}'}\right] \times (1 + \mathbf{x}\mathbf{x}')^{-m(n-1)/2} \prod_{j=1}^{p-1} x_j^{m\omega_j - 1}\, \mathrm{d}x_j \quad (15)$$

which demands evaluation.

Not surprisingly, eq 15 cannot be integrated in closed form except in special cases. For example, if $p = 2$ (a linear chain with $n = 3$, $\omega_i = 1$, or a circular chain with $n = 5$, $\omega_i = 2$, or more complicated networks) the integral reduces to a confluent hypergeometric function, and so $P(s)\,\mathrm{d}s$ is given by a known analytic function. If $p = 1$, and $\omega_1 = n - 1$, the integral in eq 7b is trivial. In such a case the Kirchoff matrix describes a molecule in which every node is connected to every other. For more interesting molecules, eq 15 at least yields the asymptotic behavior of $P(s)\,\mathrm{d}s$ for any Λ_p.

The integral over x_1 in eq 15 can be accomplished by making the change of variable

$$t = x_1^2(1 + \mathbf{x}\mathbf{x}')^{-1}$$

so that

$$F(a) = C \exp(-a\lambda_1) \int \exp(-az) \times \left(1 + \sum_2^{p-1} x_j^2\right)^{-m(n-1-\omega_j)/2} \prod_2^{p-1} x_j^{m\omega_j - 1}\, \mathrm{d}x_j \times \int_0^1 \exp(azt)(1-t)^{-m(n-1-\omega_1)/2-1} t^{m\omega_1/2-1}\, \mathrm{d}t \quad (16)$$

Choice of $\lambda_p = \max(\lambda_j)$ and $\lambda_1 = \min(\lambda_j)$ renders

$$z = \left[\lambda_p - \lambda_1 + \sum_2^{p-1} (\lambda_j - \lambda_1)x_j^2\right]\left[1 + \sum_2^{p-1} x_j^2\right]^{-1}$$

positive definite. The integral over t is[9]

$$\frac{\Gamma(m\omega_1/2)\Gamma[m(n-1-\omega_1)/2]}{\Gamma[m(n-1)/2]} M(m\omega_1/2, m(n-1)/2, az)$$

where $M(b, c, x)$ is the confluent hypergeometric function. The Kummer transformation gives

$$\exp(-az)M(m\omega_1/2, m(n-1)/2, az) = M(m(n-1-\omega_1)/2, m(n-1)/2, -az)$$

and the asymptotic expansion of $M(b, c, -x)$ as $x \to \infty$ is

$$M(b, c, -x) = \frac{\Gamma(c)}{\Gamma(c-b)} x^{-b}[1 + 0(x^{-1})]$$

Thus, as $s \to \infty$, the dependence upon $a = n\gamma s^2$ factors and

$$F(a) = F(n\gamma s^2) = G_1(\Lambda_p)s^{-m(n-1-\omega_1)} \exp(-n\gamma\lambda_1 s^2)$$

where $G_i(\Lambda_p)$ is a function of n, m, γ, and Λ_p, but not of s. The asymptotic expansion for $P(s)\,\mathrm{d}s$ is

$$P(s)\,\mathrm{d}s = G_2(\Lambda_p)s^{m\omega_1 - 1} \exp(-nm\lambda_1 s^2/2\langle l^2\rangle)\,\mathrm{d}s \quad (17)$$

For the linear chain, $\lambda_1 = 4\sin^2 \pi/2n \approx \pi^2/n^2$, $\omega_1 = 1$, so that for $m = 3$

$$P(s)\,\mathrm{d}s \sim s^2 \exp(-3\pi^2 s^2/2n\langle l^2\rangle)\,\mathrm{d}s \quad (18)$$

which coincides with the earlier results.[4,6] For the circular chain,[10] $\lambda_1 \approx 4\pi^2/n^2$ and $\omega_1 = 2$, so that as $s \to \infty$

$$P(s)\,\mathrm{d}s \sim s^5 \exp(-6\pi^2 s^2/n\langle l^2\rangle)\,\mathrm{d}s \quad (19)$$

If these expansions, eq 18 and 19, extend to smaller s than might be indicated by the derivation, then the behavior of the circular chain relative to the linear chain found by Šolc[10] is comprehensible. The larger power of s occurring in eq 19 for the circular chain tends to move the maximum of $P(s)$ to larger values of $s/\langle s^2\rangle_0^{1/2}$ than for the linear chain, and the larger factor in the exponent causes $P(s)$ to fall more rapidly with increasing $s/\langle s^2\rangle_0^{1/2}$. Regardless of this qualitative agreement with the known exact behavior of $P(s)$ for the two chains, care must be exercised in extending eq 18 or 19 into regions not commensurate with the asymptotic limit.

II. Distribution Function of the Inertial Tensor[10–16]

The inertial tensor $\mathcal{S}$ of a distribution of n identical particles with configuration in m dimensional space specified by the matrix

$$\mathbf{X} = \begin{bmatrix} x_1^1 & x_2^1 \ldots x_n^1 \\ x_1^2 & x_2^2 \ldots x_n^2 \\ \vdots & \vdots \quad\; \vdots \\ x_1^m & x_2^m \ldots x_n^m \end{bmatrix}$$

is given by

$$\mathcal{S} = n^{-1}\mathbf{X}\mathbf{X}' \quad (20)$$

if the origin of coordinates coincides with the center of mass. The potential energy of a Gaussian molecule with this configuration is

$$V/kT = \gamma \mathrm{Tr}(\mathbf{X}\mathbf{K}\mathbf{X}') = \gamma\mathbf{x}(\mathbf{K} \otimes 1_m)\mathbf{x}'$$

The inertial tensor is a symmetric matrix which is brought to $\mathbf{S} = \mathrm{diag}(S_1, S_2, \ldots, S_m)$ by a transformation with one of the matrices of the group $SO(m)$ of rank m orthogonal matrices of unit determinant according to $\mathbf{S} = \mathbf{R}\mathcal{S}\mathbf{R}' = n^{-1}\mathbf{R}\mathbf{X}\mathbf{X}'\mathbf{R}'$; $\mathbf{R} \in SO(m)$. The matrix $\mathbf{X}$ may be uniquely written as

$$\mathbf{X} = n^{1/2}\mathbf{R}'\mathbf{S}^{1/2}\mathbf{V}, \quad \mathbf{V}\mathbf{V}' = 1_m, \quad \mathbf{V}'\mathbf{V} \neq 1_n$$

by the Eckart–Young theorem;[17] here $\mathbf{S}^{1/2} = \mathrm{diag}(S_1^{1/2}, S_2^{1/2}, \ldots, S_m^{1/2})$

The probability distribution of the inertial tensor in principal axes is given by

$$P(S)\dot{S} = Z^{-1}\dot{S} \int \prod_1^m \delta\left(\sum_1^n x_j^\alpha\right) \exp[-\gamma\mathrm{Tr}(\mathbf{X}\mathbf{K}\mathbf{X}')]\dot{X}/\dot{S} \quad (21a)$$

where $\dot{X} = \dot{x} = \Pi_{\alpha,j}\, \mathrm{d}x_j^\alpha$, and $\dot{S} = \Pi_1^m\, \mathrm{d}S_\alpha$. Transformation to normal coordinates $\mathbf{Q} = \mathbf{X}\mathbf{T}$ as before gives

$$P(S)\dot{S} = Z^{-1}\dot{S} \int \exp[-\gamma\mathrm{Tr}(\mathbf{Q}_0\Lambda_0\mathbf{Q}_0')]\dot{Q}_0/\dot{S} \quad (21b)$$

where $\mathbf{Q}_0$ is the $m \times (n-1)$ matrix obtained from $\mathbf{Q}$ by striking q_n^α. As before, $Z = (\pi/\gamma)^{m(n-1)/2}|\Lambda_0|^{-m/2}$ normalizes $P(S)\dot{S}$.

In a coordinate frame with origin located at the center of mass of the system we have

$$\mathbf{S} = n^{-1}\mathbf{R}\mathbf{X}\mathbf{X}'\mathbf{R}' = n^{-1}\mathbf{R}\mathbf{Q}\mathbf{Q}'\mathbf{R}' = n^{-1}\mathbf{R}\mathbf{Q}_0\mathbf{Q}_0'\mathbf{R}' \quad (22)$$

The matrix $\mathbf{Q}_0 = \mathbf{R}'(\xi,\mathbf{O})\mathbf{U}$ (by the Eckart–Young theorem), where $\mathbf{R}' \in SO(m)$, $\mathbf{U} \in O(n-1)$, and $\xi = \mathrm{diag}(\xi_1, \xi_2, \ldots, \xi_m)$. (The reason for expression of $\mathbf{Q}_0$ in this form rather than in terms similar to that of $\mathbf{X}$ above will be apparent shortly.) Since $\mathcal{S} = n^{-1}\mathbf{Q}_0\mathbf{Q}_0$, we have $\xi^2 = n\mathbf{S}$.

The volume element $\dot{Q}_0$ belongs to the metric $\mathrm{d}\sigma^2 = \mathrm{Tr}(\mathrm{d}\mathbf{Q}_0\, \mathrm{d}\mathbf{Q}_0')$. However,[7]

$$\mathrm{d}\mathbf{Q}_0 = \mathrm{d}\mathbf{R}'(\xi,\mathbf{0})\mathbf{U} + \mathbf{R}'(\mathrm{d}\xi,\mathbf{0})\mathbf{U} + \mathbf{R}'(\xi,\mathbf{0})\,\mathrm{d}\mathbf{U} \quad (23a)$$

or

$$\mathbf{R}\,d\mathbf{Q}_0\mathbf{U}' = \delta\mathbf{R}(\boldsymbol{\xi},0) - (\boldsymbol{\xi},0)\delta\mathbf{U} + (d\boldsymbol{\xi},0) \quad (23b)$$

where $\delta\mathbf{R} = \mathbf{R}\,d\mathbf{R}' = -d\mathbf{R}\mathbf{R}' = -\delta\mathbf{R}'$ (since $\mathbf{R}\mathbf{R}' = 1_m$), and $\delta\mathbf{U} = -d\mathbf{U}\mathbf{U}' = -\delta\mathbf{U}'$ (since $\mathbf{U}\mathbf{U}' = 1_{n-1}$). Let $(\boldsymbol{\xi},0)\delta\mathbf{U} = (\boldsymbol{\xi}\delta\mathbf{u}_1, \boldsymbol{\xi}\delta\mathbf{u}_2)$, $\delta\mathbf{u}_1 = -\delta\mathbf{u}_1'$, so that

$$\mathbf{R}\,d\mathbf{Q}_0\mathbf{U}' = (d\boldsymbol{\xi} + \delta\mathbf{R}\boldsymbol{\xi} - \boldsymbol{\xi}\delta\mathbf{u}_1, -\boldsymbol{\xi}\delta\mathbf{u}_2)$$

and

$$d\sigma^2 = \mathrm{Tr}[(d\boldsymbol{\xi} + \delta\mathbf{R}\boldsymbol{\xi} - \boldsymbol{\xi}\delta\mathbf{u}_1)(d\boldsymbol{\xi} + \boldsymbol{\xi}\delta\mathbf{R}' - \delta\mathbf{u}_1'\boldsymbol{\xi}) + \boldsymbol{\xi}^2\delta\mathbf{u}_2\delta\mathbf{u}_2']$$

Reduction of this to

$$d\sigma^2 = \mathrm{Tr}[d\boldsymbol{\xi}^2 - (\delta\mathbf{R}\boldsymbol{\xi} - \boldsymbol{\xi}\delta\mathbf{u}_1)(\boldsymbol{\xi}\delta\mathbf{R} - \delta\mathbf{u}_1\boldsymbol{\xi}) + \boldsymbol{\xi}^2\delta\mathbf{u}_2\delta\mathbf{u}_2']$$

follows from the skew-symmetry of $\delta\mathbf{R}$ and $\delta\mathbf{u}_1$. The decomposition

$$\delta\mathbf{R}\boldsymbol{\xi} - \boldsymbol{\xi}\delta\mathbf{u}_1 = \tfrac{1}{2}[(\delta\mathbf{R}\boldsymbol{\xi} - \boldsymbol{\xi}\delta\mathbf{u}_1) + (\delta\mathbf{R}\boldsymbol{\xi} - \boldsymbol{\xi}\delta\mathbf{u}_1)'] + \tfrac{1}{2}[(\delta\mathbf{R}\boldsymbol{\xi} - \boldsymbol{\xi}\delta\mathbf{u}_1) - (\delta\mathbf{R}\boldsymbol{\xi} - \boldsymbol{\xi}\delta\mathbf{u}_1)']$$

into symmetric

$$\delta\mathbf{a} = \tfrac{1}{2}[(\delta\mathbf{R} + \delta\mathbf{u}_1)\boldsymbol{\xi} - \boldsymbol{\xi}(\delta\mathbf{R} + \delta\mathbf{u}_1)] = \delta\boldsymbol{\theta}\boldsymbol{\xi} - \boldsymbol{\xi}\delta\boldsymbol{\theta}, \quad \delta\boldsymbol{\theta} = -\delta\boldsymbol{\theta}'$$

and skew-symmetric

$$\delta\mathbf{b} = \tfrac{1}{2}[(\delta\mathbf{R} - \delta\mathbf{u}_1)\boldsymbol{\xi} + \boldsymbol{\xi}(\delta\mathbf{R} - \delta\mathbf{u}_1)] = \delta\boldsymbol{\phi}\boldsymbol{\xi} + \boldsymbol{\xi}\delta\boldsymbol{\phi}, \; \delta\boldsymbol{\phi} = -\delta\text{-}\boldsymbol{\phi}'$$

parts gives

$$d\sigma^2 = \mathrm{Tr}[d\boldsymbol{\xi}^2 + \delta\mathbf{a}^2 - \delta\mathbf{b}^2 + \boldsymbol{\xi}^2\delta\mathbf{u}_2\delta\mathbf{u}_2'] = \sum_{\alpha=1}^{m} d\xi_\alpha^2 + 2\sum_{\alpha<\beta}[(\xi_\alpha - \xi_\beta)^2\delta\theta_{\alpha\beta}^2 + (\xi_\alpha + \xi_\beta)^2\delta\phi_{\alpha\beta}^2] + \sum_{\alpha=1}^{m}\xi_\alpha^2\sum_{\alpha=1}^{n-m-1}\delta u_{2,\alpha j}^2 \quad (24)$$

for which the volume element is

$$\dot{Q}_0 = 2^{m(m-1)/2}\prod_{\alpha=1}^{m}\xi_\alpha^{n-m-1} \times d\xi_\alpha \prod_{\alpha<\beta}|\xi_\alpha^2 - \xi_\beta^2|\delta\theta_{\alpha\beta}\delta\phi_{\alpha\beta}\prod_{a,j}\delta u_{2,\alpha j} \quad (25)$$

Now, since

$$\begin{bmatrix}\delta\phi_{\alpha\beta}\\ \delta\theta_{\alpha\beta}\end{bmatrix} = \begin{bmatrix}\tfrac{1}{2} & -\tfrac{1}{2}\\ \tfrac{1}{2} & \tfrac{1}{2}\end{bmatrix}\begin{bmatrix}\delta R_{\alpha\beta}\\ \delta u_{1,\alpha\beta}\end{bmatrix}$$

the term

$$\prod_{\alpha<\beta}\delta\theta_{\alpha\beta}\,\delta\phi_{\alpha\beta} = 2^{-m(m-1)/2}\prod_{\alpha<\beta}\delta R_{\alpha\beta}\delta u_{1,\alpha\beta}$$

and eq 21b becomes

$$P(S)\dot{S} = |\Lambda_0|^{m/2}(n\gamma/\pi)^{m(n-1)/2}|\mathbf{S}|^{(n-m-2)/2}\prod_{\alpha<\beta} \times |S_\alpha - S_\beta|\dot{S}\int \exp[-n\gamma\mathrm{Tr}(\mathbf{S}\mathbf{U}_0\Lambda_0\mathbf{U}_0')]\delta\mathbf{R}\delta\mathbf{U}_0 \quad (26)$$

where $\mathbf{U}_0$ is the first m rows of $\mathbf{U}$. The volume elements

$$\delta\mathbf{R} = \prod_{\alpha<\beta}\delta R_{\alpha\beta}$$

and

$$\delta\mathbf{U}_0 = \prod_{\alpha<\beta}\delta u_{1,\alpha\beta}\prod_{\alpha j}\delta u_{2,\alpha j}$$

require elaboration.

Let $d\sigma^2 = \mathrm{Tr}(d\mathbf{V}\,d\mathbf{V}')$ be the metric on the space of rank l orthogonal matrices, i.e., $\mathbf{V}$ runs through all of $SO(l)$. Then

$$d\sigma^2 = \mathrm{Tr}(d\mathbf{V}\,d\mathbf{V}') = \mathrm{Tr}(d\mathbf{V}\mathbf{V}'\mathbf{V}\,d\mathbf{V}') = \mathrm{Tr}(\delta\mathbf{V}'\delta\mathbf{V})$$

where $\delta\mathbf{V} = \mathbf{V}\,d\mathbf{V}'$ is skew-symmetric. In component notation,

$$d\sigma^2 = \sum_{\alpha,\beta}\delta V_{\alpha\beta}'\delta V_{\beta\alpha} = 2\sum_{\alpha<\beta}\delta V_{\alpha\beta}^2$$

and the associated volume element is

$$2^{l(l-1)/4}\prod_{\alpha<\beta}\delta V_{\alpha\beta} = \dot{V}$$

Suppose now that $\mathbf{V}$ is partitioned into

$$\mathbf{V} = \begin{bmatrix}\mathbf{v}_1 & \mathbf{v}_2\\ \mathbf{v}_3 & \mathbf{v}_4\end{bmatrix}$$

so that

$$\delta\mathbf{V} = \begin{bmatrix}\delta\mathbf{v}_1' & -\delta\mathbf{v}_2\\ \delta\mathbf{v}_2' & \delta\mathbf{v}_4'\end{bmatrix} = \begin{bmatrix}\mathbf{v}_1\,d\mathbf{v}_1' + \mathbf{v}_2\,d\mathbf{v}_2' & \mathbf{v}_1\,d\mathbf{v}_3' + \mathbf{v}_2\,d\mathbf{v}_4'\\ \mathbf{v}_3\,d\mathbf{v}_1' + \mathbf{v}_4\,d\mathbf{v}_2' & \mathbf{v}_3\,d\mathbf{v}_3' + \mathbf{v}_4\,d\mathbf{v}_4'\end{bmatrix}$$

The metric

$$\mathrm{Tr}(\delta\mathbf{v}_1\delta\mathbf{v}_1' + \delta\mathbf{v}_2\delta\mathbf{v}_2') = \mathrm{Tr}(d\mathbf{v}_1\,d\mathbf{v}_1' + d\mathbf{v}_2\,d\mathbf{v}_2') = \mathrm{Tr}(d\mathbf{V}_0\,d\mathbf{V}_0')$$

on account of the orthogonality of $\mathbf{V}$. Here, as above, $\mathbf{V}_0 = (\mathbf{v}_1, \mathbf{v}_2)$. The volume element belonging to this metric, where now $\mathbf{V}_0 \to \mathbf{U}_0$, is

$$2^{m(m-1)/4}\cdot\prod_{\alpha<\beta}\delta u_{1,\alpha\beta}\prod_{a,j}\delta u_{2,aj} = \dot{U}_0$$

Equation 26 may now be written

$$P(S)\dot{S} = 2^{-m(m-1)/2}(n\gamma/\pi)^{m(n-1)/2} \times |\Lambda_0|^{m/2}|\mathbf{S}|^{(n-m-2)/2}\prod_{\alpha<\beta}|S_\alpha - S_\beta|\dot{S} \times \int\dot{R}\int\exp[-n\gamma\mathrm{Tr}(\mathbf{S}\mathbf{U}_0\Lambda_0\mathbf{U}_0')]\dot{U}_0 \quad (27)$$

where $\int\dot{R}$ is the volume of the orthogonal group $SO(m)$, and the integral over $\dot{U}_0$ is constrained by $\mathbf{U}_0\mathbf{U}_0' = 1_m$. This manifold is the symmetric space $SO(n-1)/SO(n-m-1)$.[8,18,19] [The group $SO(n-1)$ acts transitively on $\mathbf{U}_0$, since the point $(1_m, \mathbf{0})$ is mapped into any $\mathbf{U}_0 = (1_m, \mathbf{0})\mathbf{G}$, where $\mathbf{G} \in SO(n-1)$. Furthermore, the subgroup $SO(n-m-1)$ consisting of matrices of the type

$$\begin{bmatrix}1_m & \mathbf{0}\\ \mathbf{0} & \mathbf{H}\end{bmatrix}\mathbf{H} \in SO(n-m-1)$$

leaves $(1_m, \mathbf{0})$ fixed. These facts suffice to identity $\mathbf{U}_0$ with $SO(n-1)/SO(n-m-1)$.] The volume of $\mathcal{V}_l$ of $SO(l)$ is given by Hua[7] as

$$\mathcal{V}_l = \int\dot{V} = 2^{3l(l-1)/4}\pi^{l(l-1)/4}\prod_{\nu=1}^{l-1}\Gamma(\nu/2)/\Gamma(\nu) \quad (28)$$

The volume of $SO(l)/SO(l-k)$ is $\mathcal{V}_l/\mathcal{V}_{l-k}$, as is shown by the following argument.[7] Partition $\mathbf{V}' = (\mathbf{V}_0', \mathbf{V}_1')$, where $\mathbf{V}_0'$ is of dimension $l \times k$, $k < l$; then

$$\int_{\mathbf{V}\mathbf{V}'=1}\dot{V} = \int_{\mathbf{V}\mathbf{V}'=1}\dot{V}_0\dot{V}_1 = \int_{\mathbf{V}_0\mathbf{V}_0'=1}\dot{V}_0\int_{\substack{\mathbf{V}_1\mathbf{V}_1'=1\\ \mathbf{V}_0\mathbf{V}_1'=0}}\dot{V}_1$$

Suppose $\mathbf{V}_0$ to be fixed while integrating over $\mathbf{V}_1$. There exists a transformation $\mathbf{P}'\mathbf{V}_0\mathbf{G} = (1_k, 0)$; hence $(1_k, \mathbf{0})\mathbf{G}'\mathbf{V}_1' = \mathbf{0}$, or $\mathbf{V}_1\mathbf{G} = (\mathbf{0}, \mathbf{W})$. But $\mathbf{V}_1\mathbf{G}\mathbf{G}'\mathbf{V}_1' = \mathbf{W}\mathbf{W}' = 1_{l-k}$; furthermore $|\mathbf{G}| = 1$. Thus, $\mathbf{W} \in SO(l-k)$, and

$$\mathcal{V}_l = \int_{\mathbf{V}\mathbf{V}'=1}\dot{V} = \int_{\mathbf{W}\mathbf{W}'=1}\dot{W}\int_{\mathbf{V}_0\mathbf{V}_0'=1}\dot{V}_0 = \mathcal{V}_{l-k}\int_{\mathbf{V}_0\mathbf{V}_0'=1}\dot{V}_0 \quad (29)$$

Use of eq 28 in eq 27 yields

$$P(S)\dot{S} = (2\pi)^{m(m-1)/4} \prod_{1}^{m-1} [\Gamma(\nu/2)/\Gamma(\nu)] \times (n\gamma/\pi)^{m(n-1)/2} |\Lambda_0|^{m/2} |\mathbf{S}|^{(n-m-2)/2} \prod_{\alpha<\beta} |S_\alpha - S_\beta| \dot{S} \times \int \exp[-n\gamma \mathrm{Tr}(\mathbf{S}\mathbf{U}_0\Lambda_0\mathbf{U}_0')]\dot{\mathbf{U}}_0 \quad (30)$$

Since the integral extends over the compact space $SO(n-1)/SO(n-m-1)$, the first term of the series is

$$2^{m(2n-m-4)/2}\pi^{-m/2} \frac{\Gamma[(n-2)/2]}{\Gamma(n-2)} \prod_{\nu=1}^{m-1} \times \frac{\Gamma[(n-m-2+\nu)/2]\Gamma(\nu/2)}{\Gamma(n-m-2+\nu)\Gamma(\nu)} (2n\gamma)^{m(n-1)/2} \times |\Lambda_0|^{m/2} |\mathbf{S}|^{(n-m-2)/2} \prod_{\alpha<\beta} |S_\alpha - S_\beta| \dot{S}$$

Successive terms are not so easily calculated. However, the integral in eq 30 can be accomplished for $m = n = 2$ and results in the modified Bessel function I_0.

The integral over the manifold $\mathbf{U}_0\mathbf{U}_0' = 1$ may be reduced by insertion of a product of $m(m+1)/2$ delta functions in the analogous integral over $\mathbf{R}^{m(n-1)}$, so that

$$G(S) = \int \exp[-n\gamma \mathrm{Tr}(\mathbf{S}\mathbf{U}_0\Lambda_0\mathbf{U}_0')]\dot{U}_0 = (2\pi)^{-m(m+1)/2} \int \mathbf{dk} \exp[i\mathrm{Tr}(\mathbf{KYY}') - i\mathrm{Tr}(\mathbf{K})] \exp[-n\gamma \mathrm{Tr}(\mathbf{SY}\Lambda_0\mathbf{Y}')]\dot{Y}$$

Here $\mathbf{dk} = \Pi_{\alpha<\beta}\, \mathrm{d}k_{\alpha\beta}$, and

$$\mathbf{K} = \begin{bmatrix} \mathrm{d}k_{11} & \tfrac{1}{2}\mathrm{d}k_{12}\ldots & \tfrac{1}{2}\mathrm{d}k_{1m} \\ \tfrac{1}{2}\mathrm{d}k_{12} & \mathrm{d}k_{22} & \vdots \\ \vdots & & \\ \tfrac{1}{2}\mathrm{d}k_{1m} & \ldots & \mathrm{d}k_{mm} \end{bmatrix}$$

It is easy to show that $\mathrm{Tr}(\mathbf{SY}\Lambda_0\mathbf{Y}') = \mathbf{y}(\mathbf{S} \otimes \Lambda_0)\mathbf{y}'$, where $\mathbf{y} = (y_1^1, y_2^1, \ldots, y_{n-1}^1, y_1^2, \ldots, y_{n-1}^m)$. The integral becomes

$$G(S) = (2\pi)^{-m(m+1)/2}(\pi/n\gamma)^{m(n-1)/2} \times \int dk\, exp[-iTr(\mathbf{K})]\, |\mathbf{S} \otimes \Lambda_0 - (i/\gamma n)\mathbf{K} \otimes 1_{n-1}|^{-1/2}$$

which can be alternatively represented in polar form by transformation of $\mathbf{K}$[16]. This integral does not yet hold promise of further reduction to simple terms.

III. Discussion

The distribution function of the inertial tensor given as eq 30 provides some insight into the behavior of Gaussian molecules. For present purposes, the functional dependence

$$P(S)\dot{S} \propto |\mathbf{S}|^{(n-m-2)/2} \prod_{\alpha<\beta} |S_\alpha - S_\beta| G(\mathbf{S})\dot{S}$$

is of interest. It is first noteworthy that a Gaussian molecule is never spherically symmetric.[10–15] (More precisely stated, spherical configurations constitute a set of measure zero.) The basis of this well-known behavior can be explained in elementary terms. Take the case $m = 3$; the space of all ellipsoids with axes a_1, a_2, a_3 fills an octant of $\mathbf{R}^3$. The space of all spheres is the line $a_1 = a_2 = a_3$. The measure of the former space is infinitely larger than that of the latter. The C_{3v} symmetry axis of the octant is the line on which spheres reside, and the molecule will appear to be spherical only if the configurations are averaged over all orientations relative to a space-fixed frame.

The second point to be emphasized is that the pronounced asymmetry of the distribution found by Šolc and Stockmayer[11,12] has a curious origin. The function $G(S)$ is a symmetric function of $S_1, \ldots, S_m$, as can be seen by permuting a pair of the S_α in the integral. Concomitant permutation of the rows of $\mathbf{U}_0$ obviously leaves $G(S)$ unchanged. The factor in $P(S)\dot{S}$ which generates asymmetry is $\Pi_{\alpha<\beta}|S_\alpha - S_\beta|$; its effect is to restrict the range of and order the S_α. Thus, for $m = 3$, all configurations of nonzero measure are such that $0 < S_3 < S_2 < S_1 < \infty$. It is the fact that S_3 *must* be less than S_2 that makes S_3 small. Since S_1 has no upper limit, its average value is relatively large.

Review of the derivations of eq 30 suggests that these qualitative considerations have validity beyond the strictures of the Gaussian model, since they arise solely from the effect of the transformation of the configuration space to polar form. In other words, entropy is sufficient to spread the distribution of particles comprising an otherwise spherical body into ellipsoidal configurations which far outnumber those available to the parent sphere.

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